UDC 666.7:622.693.25.004.8

CERAMIC MATERIALS BASED ON TAILINGS FROM ENRICHMENT OF VERMICULITE AND APATITE – NEPHELINE ORES

O. V. Suvorova,[1,2] D. V. Makarov,[1] and V. E. Pletneva[1]

Translated from *Steklo i Keramika*, No. 7, pp. 22 – 24, July, 2009.

The possibilities of obtaining construction ceramic based on tailings from the enrichment of vermiculite and apatite-nepheline ores are investigated. Ceramic mixes which have promise for manufacturing facing tiles as well as solid and hollow brick with improved physical – mechanical properties are proposed.

Key words: waste recovery, enrichment tailings, vermiculite and apatite-nepheline ore, ceramic mixes, tile, brick.

The volume of stacked mining wastes is comparable to the industrial demand for mineral ores in the construction materials industry. However, only 5 – 8% of the wastes are currently being utilized [1]. One promising use for technogenic raw materials, specifically, the enrichment tailings, is in manufacturing of construction ceramic by liquid sintering.

Enormous stocks of tailings from the enrichment of various ores — potential material for the production of ceramic — have accumulated near transport arteries in regions of Murmansk Oblast with quite well-developed infrastructure. Recovery of these waste products is oriented toward solving ecological problems of the region, improving living conditions for the general public, and creating additional jobs. Ceramic brick is not being manufactured at the present time in Murmansk Oblast. As a result the the brick shipped into the region is appreciably more expensive than in the central regions of the European part of the Russian Federation.

The possibility of obtaining construction ceramic based on tailings from the enrichment of vermiculite and apatite-nepehline ores is studied in the present work.

Olivine (forsterite) and diopside predominate in the tailings from the enrichment of vermiculite ores. Vermiculite, apatite, and magnetite are present in appreciable quantities. The diffraction pattern of a tailings sample is displayed in Fig. 1.

The main component of the finely dispersed waste products from the enrichment of apatite-nepheline ores is nepheline (55 – 65%[3]). We used apatite flotation tailings as a component in ceramic mixes. A typical diffraction pattern of a tailings sample is displayed in Fig. 1. Nepheline predominates in the composition; ancillary minerals — natrolite and hydromica — are also recorded. The chemical composition

[1] Institute of the Russian Academy Sciences "I. V. Tananaev Institute of Chemistry and Technology of Rare-Earth Elements and Mineral Resources" of the Kola Center for Science of the Russian Academy of Sciences, Apatity, Russia.

[1] E-mail: suvorova@chemy.kolasc.net.ru.

[3] Here and below — content by weight.

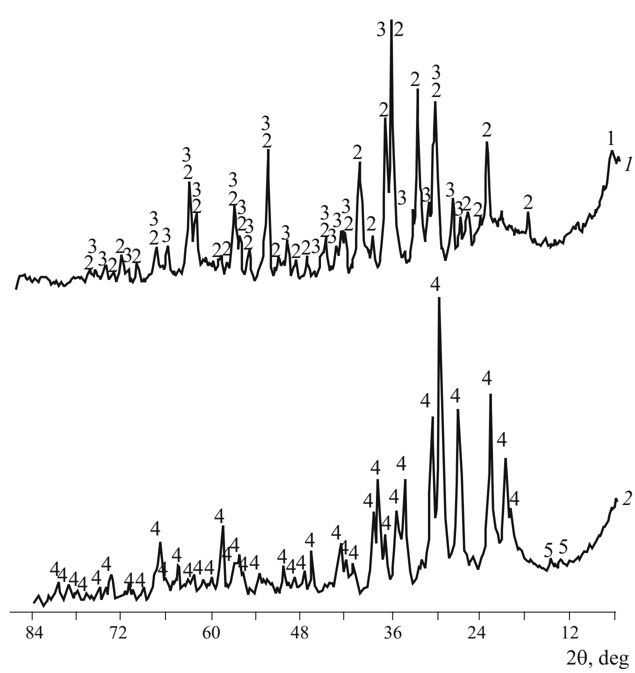

Fig. 1. Diffraction pattern of tailings from the enrichment of vermiculite (*1*) and apatite-nepheline (*2*) ores; *1*) vermiculite; *2*) forsterite; *3*) diopside; *4*) nepheline; *5*) natrolite.

TABLE 1.

Waste products composition	Content, wt.%											
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	MnO	Na_2O	K_2O	P_2O_5	other
1	41.00	4.52	20.00	6.89	2.46	6.12	1.43	0.25	8.76	4.73	1.80	0.96
2	35.30	0.15	0.89	0.79	3.32	15.64	34.28	0.12	0.26	0.08	5.58	3.30

TABLE 2.

Mix composition	Content, wt.%											
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	MnO	Na_2O	K_2O	P_2O_5	other
1	42.34	0.57	2.71	1.32	2.91	13.12	27.57	0.12	1.09	0.54	4.64	2.74
2	42.91	1.01	4.62	1.93	2.81	12.17	24.28	0.13	1.93	1.00	4.27	2.50
3	46.43	1.22	5.53	2.20	2.61	10.91	20.93	0.13	2.35	1.23	3.80	2.22
4	49.95	1.44	6.45	2.46	2.40	9.66	17.57	0.14	2.76	1.46	3.33	1.94
5	53.47	1.64	7.36	2.73	2.19	8.40	14.21	0.14	3.17	1.69	2.86	1.66

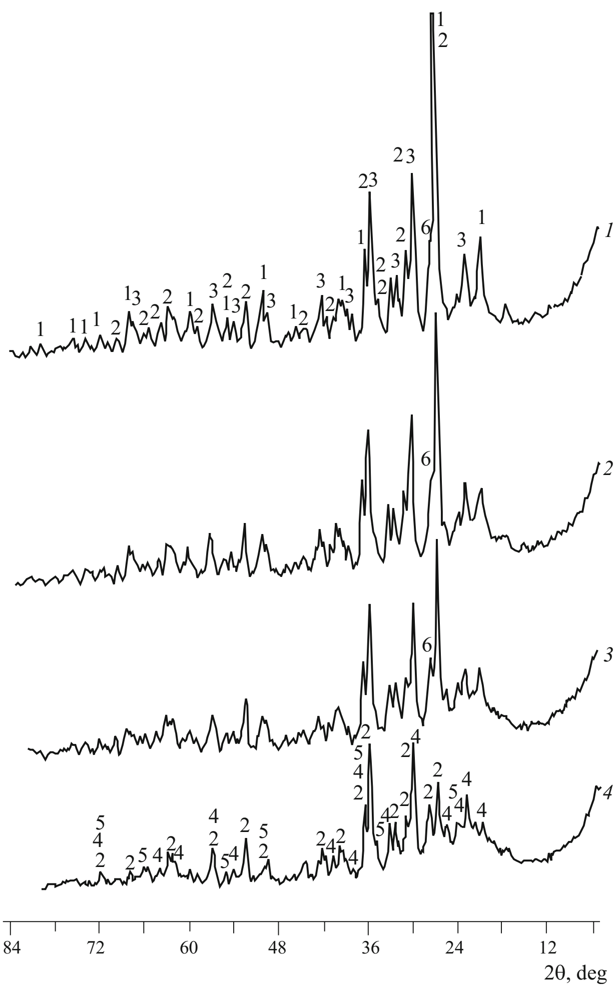

Fig. 2. X-ray diffraction pattern of samples with composition 4, fired at temperatures 900 (*1*), 950 (*2*), 1000 (*3*), and 1050°C (*4*): *1*) quartz; *2*) diopside; *3*) nepheline; *4*) forsterite; *5*) hematite; *6*) albite.

of the enrichment tailings of apatite-nepheline (composition 1) and vermiculte (composition 2) ores is presented in Table 1. Quartz is used as the third component in the mixes.

The raw materials components were comminuted to specific surface area 3000 cm^2/g. The mixture was carefully homogenized, moistened to optimal moisture content, and molded by pressing with specific pressure 20 MPa. A sulfite – alcohol mash was used in the amount 0.5% as a temporary binder to impart strength to the green compact. After drying at 105°C the samples were fired at 900 – 1100°C with isothermal soaking for 0.5 – 5 h. The samples were allowed to cool in the furnace over a period of 8 h. The fired samples were tested for compression and bending strength. In addition, the average density, porosity, water absorption, and shrinkage were determined. The chemical resistance, frost resistance, and thermal conductivity were determined for individual samples.

The theoretical composition of the high-temperature mineral phases was calculated from the chemical composition of the mixes, which is presented in Table 2. However, such a mineral composition would occur only if complete equilibrium is reached. In real ceramic mixes complete equilibrium is not attained during firing, only local equilibria are established. The more finely dispersed and homogeneous the materials are, the closer the ceramic sinter is to an equilibrium state.

When ceramic is fired a large fraction of the product remains in the solid state. As a result diffusion plays an important role in the establishment of equilibrium. Like the ratio of the solid phase and melt, the diffusion rate depends on the firing temperature. Consequently, we performed x-ray phase and microscopic studies of the ceramic sinters for different firing temperatures ranging from 900 to 1050°C.

As an example we shall examine the XPA results obtained for sample 4. Nepheline was still found in the ceramic

TABLE 3.

Mix composition	Firing temperature, °C	Average density, g/cm^3	Porosity, %	Shrinkage, %	Ultimate strength, MPa		Water absorption, %	Frost resistance, cycles
					under compression	under bending		
1	1050	2.14	29.8	0.9	56.3	18.0	11.1	> 50
	1100	2.25	28.3	2.2	118.7	27.6	10.7	> 50
2	1050	2.15	29.0	1.4	97.9	15.0	15.5	> 50
3	1050	2.17	26.7	0.9	98.6	20.2	14.0	> 50
4	950	1.96	34.8	0.0	39.2	5.8	17.9	> 50
	1000	2.01	32.6	2.0	76.1	13.8	16.1	> 100
	1050	2.03	22.1	6.3	101.0	22.5	8.6	> 100
5	950	1.87	36.1	0.9	45.8	7.1	19.6	> 50
	1000	2.07	31.5	4.5	78.8	14.4	13.5	> 100
	1050	2.52	20.0	10.8	152.6	29.4	3.4	> 100
	1100	2.08	–	–	158.9	42.5	0.1	–

sinter after firing at 900°C. The quartz and diopside reflections are the strongest reflections in the diffraction pattern. The phases represented by albite are formed in the reaction

$$NaAlSiO_4 + 2SiO_2 = NaAlSi_3O_8.$$

However, the latter phase is not definitively identified because the reflections of other minerals are superposed. In addition, several weak unidentified reflections are noted; they could be due to extrinsic minerals (Fig. 2).

Quartz reflections remain in the diffraction pattern samples fired at 950°C; albite reflections are sharper. Melt formation is seen more distinctly at this temperature, to which not only microscopic studies but also the appearance of a characteristic halo in the x-ray diffraction pattern attest.

The intensity of the quartz reflections already decreases noticeably after firing at 1000°C. Finally, after firing at 1050°C the quartz reflections disappear completely and only the reflections due to diopside, forsterite, and hematite remain. The remaining minerals pass into the melt.

The physical – mechanical properties of some ceramic materials obtained under optimal conditions are presented in Table 3.

The mixes with compositions 1 – 3 comply with the requirements for ceramic facing tiles. The mixes with the compositions 4 and 5 can be recommended for obtaining wall construction ceramic — solid and hollow brick with improve mechanical characteristics and higher frost resistance (more than 50 cycles).

The nonmagnetic fraction of the tailings from the enrichment of vermiculite ores was used, and in addition 2 – 4% carbon was added to the mix to decrease the thermal conductivity of the materials. This decreased the thermal conductivity of the material to 0.37 W/(m · K) for the material made from the mix with composition 4 — nonmagnetic fraction + 2% carbon and firing at 950°C and to 0.34 W/(m · K) for mix with composition 5 — nonmagnetic fraction + 4% carbon and firing at 950°C.

In addition, the acid resistance was measured for a number of compositions. For example, after firing at 1100°C the acid resistance is 89.5% for ceramic made from the mix with composition 4 and 93.2% for composition 5.

In summary, ceramic mixes which have promise for manufacturing facing tiles and brick with improved physical – mechanical properties have been obtained using the tailings from enrichment of vermiculite and apatite-nepheline ores.

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